JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 113, G03037, doi:10.1029/2008JG000701, 2008

Molecular hydrogen uptake by soils in forest, desert, and marsh ecosystems in California

Nicole V. Smith-Downey,[1,2] James T. Randerson,[3] and John M. Eiler[1]

Received 29 January 2008; revised 12 June 2008; accepted 30 June 2008; published 23 September 2008.

[1] The mechanism and environmental controls on soil hydrogen (H_2) uptake are not well understood but are essential for understanding the atmospheric H_2 budget. Field observations of soil H_2 uptake are limited, and here we present the results from a series of measurements in forest, desert, and marsh ecosystems in southern California. We measured soil H_2 fluxes using flux chambers from September 2004 to July 2005. Mean H_2 flux rates and standard deviations were $-7.9 + -4.2$, $-7.6 + -5.3$ and $-7.5 + -3.4$ nmol m^{-2} s^{-1} for the forest, desert, and marsh, respectively (corresponding to deposition velocities of $0.063 + -0.029$, $0.051 + -0.036$, $0.035 + -0.013$ cm s^{-1}). Soil profile measurements showed that H_2 mixing ratios were between 3% and 51% of atmospheric levels at 10 cm and that the penetration of H_2 into deeper soil layers increased with soil drying. Soil removal experiments in the forest demonstrated that the litter layer did not actively consume H_2, the removal of this layer increased uptake by deeper soil layers, and the exposure of subsurface soil layers to ambient atmospheric H_2 levels substantially increased their rate of uptake. Similar soil removal experiments at the desert site showed that extremely dry surface soils did not consume H_2 and that fluxes at the surface increased when these inactive layers were removed. We present a model of soil H_2 fluxes and show that the diffusivity of soils, along with the vertical distribution of layers that actively consume H_2 regulate surface fluxes. We found that soil organic matter, CO_2 fluxes, and ecosystem type were not strong controllers of H_2 uptake. Our experiments highlight H_2 diffusion into soils as an important limit on fluxes and that minimum moisture level is needed to initiate microbial uptake.

Citation: Smith-Downey, N. V., J. T. Randerson, and J. M. Eiler (2008), Molecular hydrogen uptake by soils in forest, desert, and marsh ecosystems in California, *J. Geophys. Res.*, *113*, G03037, doi:10.1029/2008JG000701.

1. Introduction

[2] The uptake of molecular hydrogen (H_2) by soils accounts for 62% to 92% of the total atmospheric H_2 sink [*Novelli et al.*, 1999; *Gerst and Quay*, 2001; *Hauglustaine and Ehhalt*, 2002; *Rahn et al.*, 2003; *Rhee et al.*, 2006; *Price et al.*, 2007; *Xiao et al.*, 2007]. Relatively few field measurements of soil H_2 uptake are available to improve these estimates. Recently, the atmospheric H_2 budget has received substantial attention because of the possibility of increased tropospheric H_2 emissions and subsequent decreases in stratospheric ozone in a hydrogen economy [*Schultz et al.*, 2003; *Tromp et al.*, 2003; *Warwick et al.*, 2004]. Current understanding of the mechanisms regulating the H_2 soil flux is limited, making it difficult to predict how the soil sink will respond to future increases in emissions or changes in climate.

[3] The uptake of H_2 by soils is a biological process that is inhibited at very low soil moisture levels [*Fallon*, 1982; *Conrad and Seiler*, 1985; *Smith-Downey et al.*, 2006] and decreases at high soil moisture levels because of limitation of H_2 diffusion into soils [*Yonemura et al.*, 1999, 2000b]. The temperature dependence of the surface flux of H_2 into soils is not consistent between field studies, and in many cases there is no observable relationship between soil temperature and H_2 flux. Laboratory measurements suggest that H_2 uptake is sensitive to changes in temperature from -4°C to 15°C, after which a broad temperature optimum is observed [*Smith-Downey et al.*, 2006]. Field measurements of soil H_2 uptake have been conducted in boreal forest ecosystems in Alaska [*Rahn et al.*, 2002] and Finland [*Lallo et al.*, 2008], savanna ecosystems in South Africa [*Conrad and Seiler*, 1985], temperate urban ecosystems in Europe [*Conrad and Seiler*, 1985], and temperate forest and agricultural ecosystems in Japan [*Yonemura et al.*, 1999, 2000a]. Additional field observations of H_2 uptake by soils are needed to more fully describe the response of soil H_2 uptake to changing environmental conditions.

[4] Here we describe a series of field experiments conducted in three different California ecosystems between September 2004 and July 2005. We measured H_2 fluxes

[1] Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA.
[2] Now at School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA.
[3] Department of Earth System Science, University of California Irvine, Irvine, California, USA.

0148-0227/08/2008JG000701$09.00

Table 1. Field Site Characteristics

				January		July		
	Latitude	Longitude	Elevation (m)	Mean High Temperature[a] (°C)	Mean Low Temperature[a] (°C)	Mean High Temperature[a] (°C)	Mean Low Temperature[a] (°C)	Mean Annual Precipitation (cm)[a]
Forest	33.81° N	116.79° W	1650	11.8	~2.5	29.5	11.1	64.6
Desert	34.15° N	116.45° W	1100	17.2	2.1	40.8	22.1	10.6
Marsh	33.66° N	117.85° W	2	17.4	8.3	22.3	16.9	28.5

[a]From the Western Regional Climate Center station observations from Idyllwild, California (forest), Twentynine Palms, California (desert), and Newport Beach, California (marsh) [*Western Regional Climate Center*, 2007]. Data were averaged over the period July 1948 to June 2007 for Idyllwild and Twentynine Palms and from November 1934 to June 2007 for Newport Beach.

and vertical profiles of H_2 mixing ratio in soils at forest, desert and marsh field sites. We performed a series of soil removal experiments to determine the uptake capacity of soil layers at different depths. CO_2 fluxes were also measured at the forest and desert sites and continuous measurements of soil temperature and soil moisture were recorded after February 2005. We found that H_2 fluxes did not depend strongly on ecosystem type and that diffusion of H_2 through dry, inactive surface soil layers limited flux rates.

2. Methods

2.1. Site Descriptions

[5] We measured hydrogen uptake by soils at three sites in Southern California (Table 1) from September 2004 to July 2005. These sites were a mixed conifer and hardwood forest ecosystem in the University of California (UC) James San Jacinto Mountain Reserve (33.81° N, 116.79° W), a desert shrub ecosystem in the UC Burns Piñon Ridge Reserve (34.15° N, 116.45° W), and a freshwater marsh in the UC San Joaquin Freshwater Marsh Reserve (33.66° N, 117.85° W), hereafter referred to as the forest, desert and marsh sites respectively. The overstory canopy at the forest site was dominated by ponderosa pine (*Pinus ponderosa*), California black oak (*Quercus kelloggii*), interior live oak (*Quercus wislizeni*) and incense cedar (*Calocedrus decurrens*). The sparse desert vegetation was largely composed of piñon pine (*Pinus monophylla)*, junipers (*Juniperus californica*), Muller's oak (*Quercus cornelius*), and cholla (*Cylindropuntia echinocarpa*). The two marsh sites we first sampled were dominated by cattail (*Typha latifolia*), and the third marsh site we sampled near the edge of a seasonal pond had both cattail and willow (*Salix*) species. The mineral soil component of the forest and desert soils were primarily sand and coarse sand, whereas the marsh soil was clay with a surface organic layer that was approximately 20 cm deep.

[6] At the forest site, three replicate soil collars and soil gas samplers were installed near a streambed and on a south-facing hillside. At the desert site, two replicate soil collars and soil gas samplers were installed at three locations along a gradient from high to low soil organic matter (SOM) content (Table 2). The collars with the highest SOM were located directly under an oak (*Quercus cornelius-mulleri*), the intermediate SOM collar were located ~2m from the oak center, and the low SOM collars were located in bare sand, ~5m from the oak center. At the marsh site, three replicate soil collars and soil gas samplers were installed first near a seasonal pond and in a reed dominated marsh. Depth to the water table was approximately 40 cm at site 1 at the marsh in October 2004. In February 2005, both of the marsh sites flooded, so a third site was established near the edge of a seasonal pond in April 2005.

2.2. Flux Measurements

[7] Soil collars were constructed from 20 cm diameter polyvinyl chloride (PVC) pipe cut into 10 cm deep sections and fitted with an acrylic collar (Figure 1a). These collars were permanently installed at each site and remained in place throughout the duration of our field measurements. A flux chamber was constructed from acrylic and included a syringe port for removal of gas samples. A 1/4″ thick Viton O-ring was placed between the soil collar and the flux chamber and the chamber was clamped to the soil collar during flux experiments to ensure a tight seal. Once the collars were capped with the flux chamber, 10 mL gas samples were withdrawn immediately (after flushing the syringe twice), and at 1, 2, 4, and 8 min intervals using plastic syringes fitted with three way nylon stopcock valves with a high-density polyethylene (HDPE) plug (Kimble-Kontes, Vineland, New Jersey).

[8] The syringes were stored on a layer of bubble wrap in a cooler filled with dry ice. Storing the samples at subzero temperatures preserved the hydrogen mixing ratio for several hours, and laboratory tests showed a leak rate of approximately 2 ppb/h for syringes filled with hydrogen free air. All samples were immediately returned to the lab and measured on the same night of sample collection. All measurements were subsequently corrected for this leak rate using the time interval between sample collection and measurement. Samples were injected into a TA3000R Reducing Gas Analyzer (Ametek Process Instruments, Newark, DE) through a 5 mL sample loop connected to a six port valve (Valco Instruments, Houston, Texas). The TA3000R RGA is a continuous flow instrument with a

Table 2. Soil Composition at Field Sites

Site	Soil Layer	Ca (%)	Na (%)	C/N[a]
Forest streambed	litter	47.5	0.81	59
Forest streambed	soil (0–5 cm)	19.4 ± 24.2	0.49 ± 0.58	39
Forest hillside	litter	50.4	1.03	49
Forest hillside	soil (0–5 cm)	1.1 ± 0.6	0.05 ± 0.02	23
Desert high SOM	litter	28.4 ± 8.2	0.09 ± 0.32	32
Desert high SOM	soil (0–5 cm)	1.2 ± 0.2	0.10 ± 0.01	13
Desert medium SOM	litter	12.3 ± 1.9	0.57 ± 0.12	22
Desert medium SOM	soil (0–5 cm)	4.2 ± 3.8	0.25 ± 0.21	17
Desert low SOM	litter	–	–	–
Desert low SOM	soil (0–5 cm)	0.1 ± 0.01	0.01 ± 0.00	13
Marsh site 3	soil (0–5 cm)	9.2 ± 0.5	0.66 ± 0.01	14

[a]Soil carbon (C) and nitrogen (N) contents measured with an elemental analyzer, Carlo Erba, Lakewood, New Jersey.

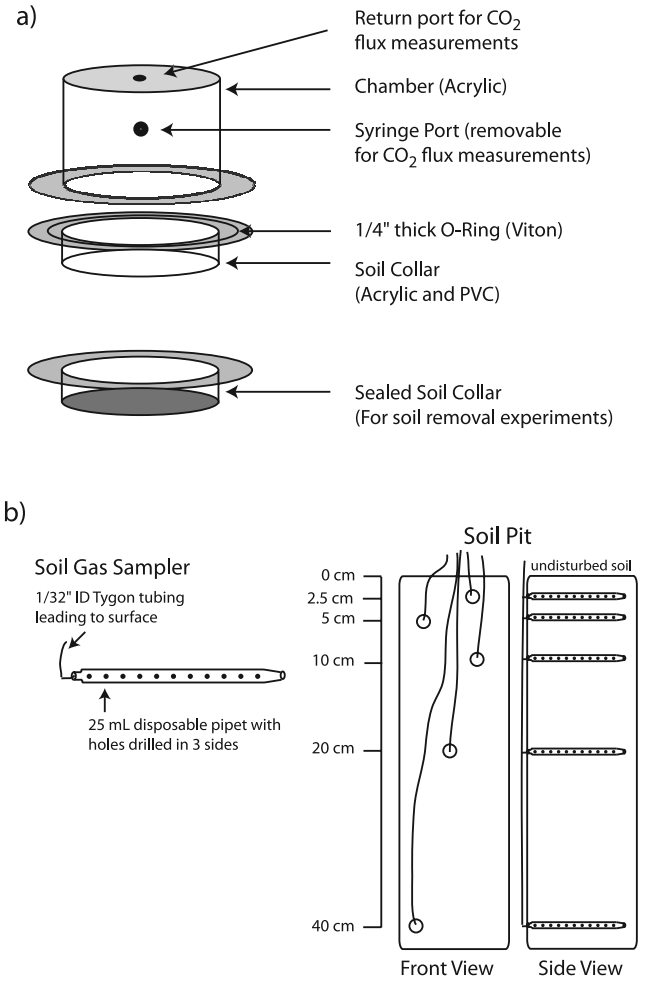

Figure 1. (a) Schematic of soil flux chamber and soil collar designs. Soil collars were 10 cm deep with a diameter of 20 cm. The flux chamber had an internal volume of 0.132 m^3. (b) Schematic of soil gas sampler design and placement.

Unibead 1S and an MS 13X column for separation of H_2 and CO.

[9] Exponential curves were fit to the H_2 mixing ratio time series obtained for each chamber flux measurement (e.g., Figure 2)

$$H_2(t) = H_2(0)e^{-bt}, \tag{1}$$

where t is time, and the flux of hydrogen into the soil (nmol m^{-2} s^{-1}) was calculated as

$$F_{H_2} = H_2(0)(-b)\frac{P}{RT}\frac{V}{A}, \tag{2}$$

where $H_2(0)$ is the mixing ratio of H_2 at t = 0 s, P is atmospheric pressure (Pa) at each site, V is the volume of the flux chamber including the space between the collar edge and the soil surface, R is the gas constant, T is temperature (K), A is the area inside the soil collar (0.0324 m^2), and b is the constant from equation (1). To normalize for the effect of the initial concentration of H_2 on the relative flux rates, we also calculated deposition velocities (cm s^{-1}), which are independent of surface concentration as

$$V_d = (-b)\frac{V}{A}. \tag{3}$$

[10] For soil CO_2 flux measurements, the same soil collars were used but the syringe port was removed from the flux chamber and replaced with a 1/4″ tube fitting that allowed continuous circulation of air through the chamber. A 0.5 L/min pneumatic pump (KNF Neuberger, Trenton, New Jersey) pulled air from the flux chamber through a filter, a LI-800 Gas Hound CO_2 analyzer (Licor, Lincoln, Nebraska) and finally pushed air back into the flux chamber through a tube fitting at the top of the chamber. The CO_2 efflux was measured for approximately 3 min and the mixing ratio of CO_2 increased linearly with respect to time. The CO_2 flux rate was calculated as

$$F_{CO_2} = m\frac{PV}{RT}\frac{1}{A}, \tag{4}$$

where P, V, R, T, and A are defined as noted above, and m is the slope of the CO_2 mixing ratio time series from the chamber.

2.3. Soil Profiles

[11] Soil profiles of H_2 concentration with depth were measured using soil gas samplers that were buried and left in place over the entire course of our field study (Figure 1b). The gas samplers were constructed from 25 mL disposable plastic pipets with 1/8″ holes drilled in three sides and 1/32″ inner diameter Tygon tubing leading to the surface. We dug soil pits to ~50 cm depth, and used a soil corer to remove horizontal plugs of soil at 2.5, 5, 10, 20 and 40 cm depth along the open face of the pit. The soil gas samplers were placed horizontally into the holes (into undisturbed soils)

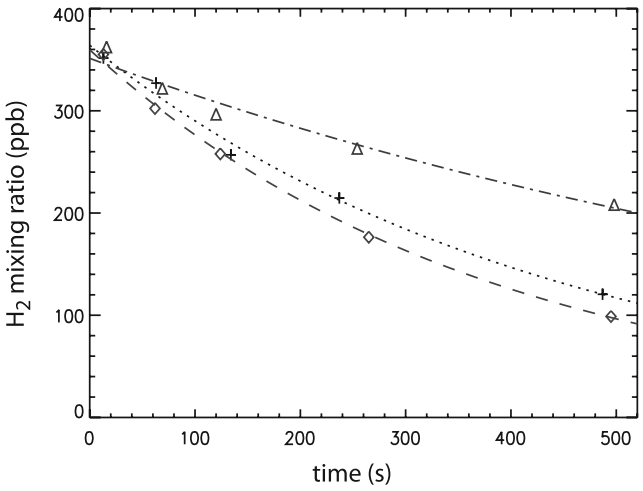

Figure 2. H_2 mixing ratio over time during three replicate flux chamber experiments at the forest streambed site on 4 November 2004. Each line is an exponential fit to the H_2 data as described by equation (1). The mean flux rate for these data was −9.8 ± 3.7 nmol m^{-2} s^{-1}.

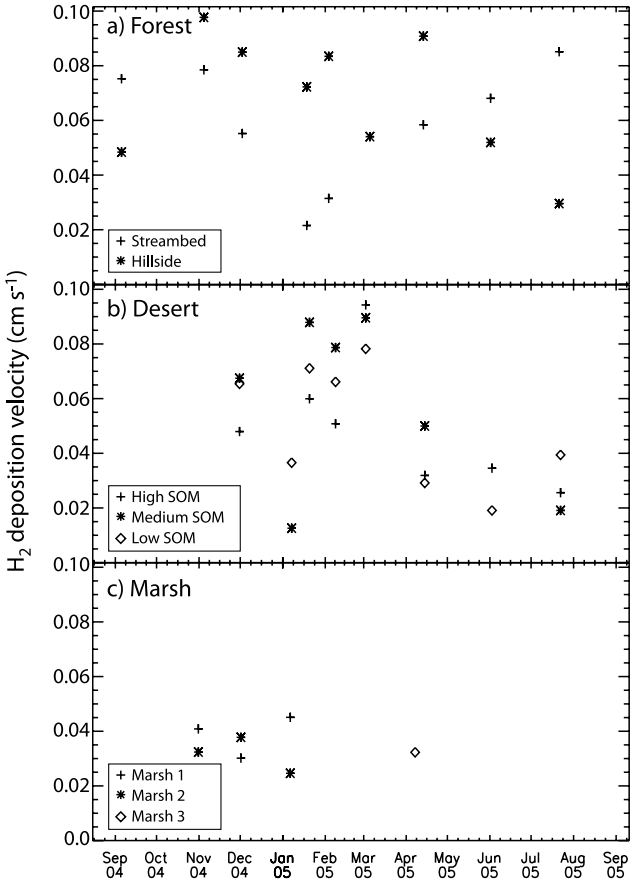

Figure 3. H_2 deposition velocities (cm s^{-1}) at the (a) forest, (b) desert, and (c) marsh field sites spanning September 2004 to July 2005. A deposition velocity of 0.05 cm s^{-1} is equivalent to a flux of −11.0 nmol m^{-2} s^{-1}, assuming that $H_2(0)$ = 530 ppb, T = 293 K. and P = 101325 Pa.

and the pit was back filled with tubes leading to the surface. Soil gas samples were extracted with 10 mL plastic syringes fitted with a three way valve and a luer stub adaptor (BD, Franklin Lakes, New Jersey). First, 5 mL of air was removed from the gas samplers and was flushed out of the syringe and valve, then a full 10 mL was withdrawn, the valve was closed, and the syringes were placed on bubble wrap in a dry ice filled cooler.

2.4. Soil Removal Experiments

[12] We conducted a series of soil removal experiments at the forest and desert sites in April of 2005. A 30 cm deep soil collar was inserted into the soil near the hillside site (forest) and in a low SOM area (desert) and the H_2 flux was measured as described in section 2.2. Next, the vegetation contained in the collars was removed, and placed in a separate soil collar with a plastic dish glued to the bottom (Figure 1a). We capped the sealed soil collar with the flux chamber and measured the H_2 flux in the chamber. The flux chamber was moved back to the intact soil collar, where we remeasured the flux of H_2 in the soil collar, then removed a few cm of soil. The removed soil was placed in the sealed collar and the H_2 flux was measured. This process was repeated to establish the H_2 uptake capacity of individual soil layers (and of the remaining soil profile as layers were removed).

2.5. Soil Properties

[13] We measured the temperature of soils at 5 and 10 cm depth at each soil collar during each flux experiment. Soil samples from the top 5 cm were also collected near the collars, sealed in plastic vials and frozen. These samples were later used to calculate volumetric water content of the surface soils. Soil samples collected in September 2005 were analyzed for percent C and N.

[14] Soil temperature and moisture were measured continuously after February 2005 at the forest and desert sites using integrating temperature sensors from 0 to 5 cm depth (Model 107-L, Campbell Scientific, Logan, UT) and time domain reflectometry (TDR) sensors at 5 and 20 cm depth (Model 616-L, Campbell Scientific, Logan, UT). Data were averaged every 1/2 h and stored on CR10X data loggers (Campbell Scientific, Logan, UT). Southern California received an anomalously high amount of precipitation over the winter of 2005, and our sites received 100 cm (forest), 21 cm (desert), and 40 cm (marsh) of precipitation between September 2004 and May 2005 (Western Regional Climate Center (WRCC) station observations from Idyllwild, California, Twentynine Palms, California, and Newport Beach, California [*WRCC*, 2007]).

3. Field Results

[15] The loss of H_2 from the chamber headspace was initially quite rapid, and slowed as the mixing ratio of H_2 in the chamber decreased. The H_2 flux was therefore modeled as first-order loss process using a negative exponential relationship (equation (1)). An example time series from the forest site on 4 November 2004 is shown in Figure 2. The forest and desert H_2 fluxes exhibited similar ranges of variability with deposition velocities ranging from 0.01 to 0.1 cm s^{-1} (Figure 3). No clear seasonal pattern was evident in our data. We observed substantially smaller deposition velocities in the forest streambed site in January 2005 due to a flooding event that deposited ~5 cm of litter and sediment over our collars (Figure 3a). The deposition velocities recovered to preflood levels by April 2005. In March 2005, H_2 deposition velocities at the desert site were substantially higher than at any other time (Figure 3b), and corresponded to a period when soil moisture remained relatively high and soil temperatures were relatively warm (Figure 4). Deposition velocities at the marsh were generally lower (0.015 to 0.054 cm s^{-1}) than at the forest and desert sites and were less variable (Figure 3c). Mean H_2 flux rates and standard deviations were −7.9 ± 4.2, −7.6 ± 5.3 and −7.5 ± 3.4 nmol m^{-2} s^{-1} for the forest, desert, and marsh, respectively (Table 3).

[16] CO_2 fluxes were consistently higher at the forest streambed site than the hillside site (Figure 5a and Table 3) and the organic carbon content of the streambed soils was higher than that of the hillside (Table 2). At the desert site, mean CO_2 fluxes were a factor of 5 higher in the high SOM collars than in the low SOM collars (Tables 2 and 3 and Figure 5), but no similar pattern existed for H_2 fluxes. Soil temperature steadily increased at the forest and desert sites

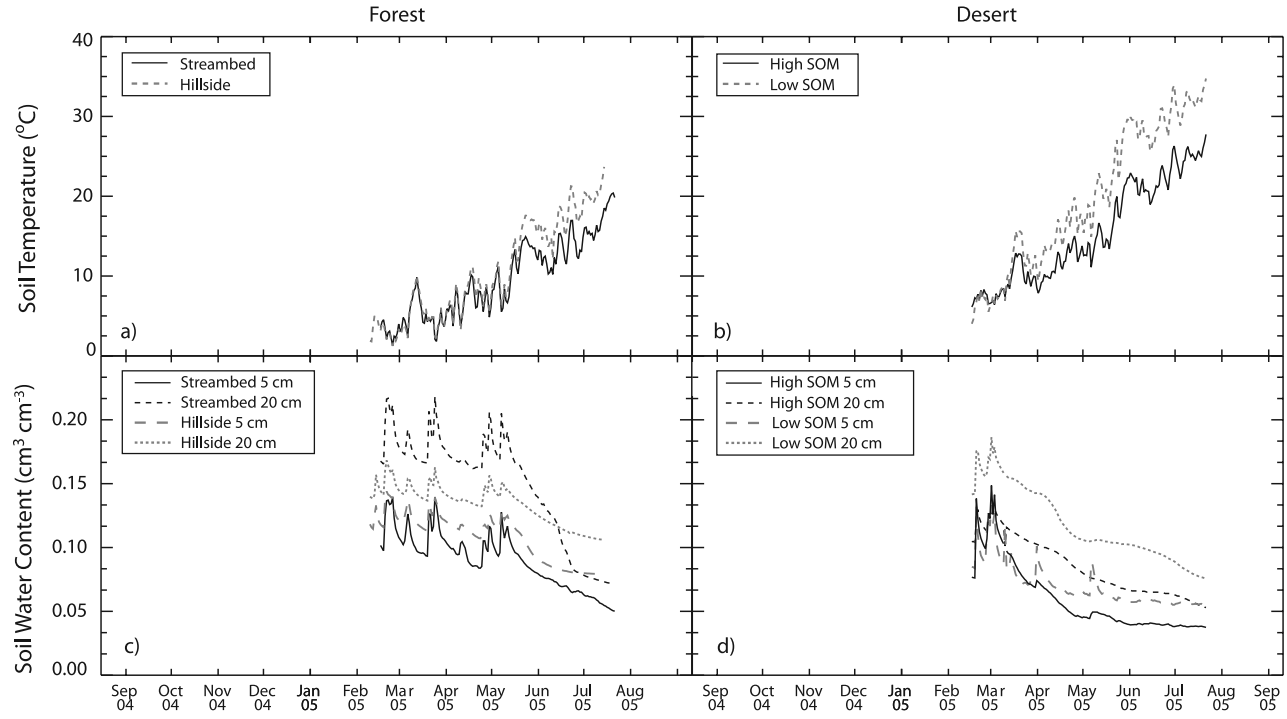

Figure 4. Mean daily soil temperature (°C) for the top 5 cm of soil at the (a) forest and (b) desert field sites measured with integrating soil temperature sensors. Mean daily volumetric water content (cm^3 cm^{-3}) for the (c) forest and (d) desert field sites at 5 and 20 cm depth measured with time domain reflectrometry (TDR) probes.

between January and July (Figures 4a and 4b). Volumetric water content of soils decreased at the forest site after the last rain event in May 2005 (Figure 4c). Soil moisture decreased at the desert site after March 2005 (Figure 4d). At both sites the soil moisture was higher at 20 cm depth than at 5 cm depth.

[17] Our soil profile measurements showed that, at the forest and desert sites, average H_2 mixing ratios decreased rapidly with depth, were between 3% and 51% of atmospheric levels at 10 cm, and were always less than 10% of atmospheric levels at 40 cm (Figure 6). From March 2005 through July 2005, H_2 at the desert site penetrated progressively deeper into the soil profile. This coincided with decreases in surface H_2 fluxes (Figure 7a). The mixing ratio of H_2 at 5 cm depth increased along with a decrease in the volumetric water content of soils (Figure 7b), and surface fluxes decreased as the volumetric water content at 5 cm depth decreased (Figure 7c). A similar, although smaller change, occurred at the forest hillside site in July 2005. Soil H_2 mixing ratios at a depth of 40 cm were substantially higher at the marsh site (Figure 6c), which may be due to the anaerobic production of H_2 in saturated soils below our deepest soil gas sampler.

[18] At the forest site, soil removal experiments showed that grass and litter layers did not significantly contribute to

Table 3. Mean H_2 and CO_2 Fluxes at Field Sites

Site	Mean H_2 Flux (nmol m^{-2} s^{-1}) [Deposition Velocity] (cm s^{-1})	Mean CO_2 Flux (mmol m^{-2} s^{-1})
Forest streambed	−7.8 ± 4.2 [0.060 ± 0.027]	7.6 ± 2.4
Forest hillside	−8.0 ± 4.3 [0.065 ± 0.031]	3.6 ± 1.8
Desert high SOM	−6.8 ± 3.1 [0.048 ± 0.022]	3.3 ± 1.6
Desert medium SOM	−8.3 ± 7.5 [0.053 ± 0.053]	1.4 ± 0.8
Desert low SOM	−7.6 ± 4.6 [0.052 ± 0.029]	0.6 ± 0.5
Marsh all sites	−7.5 ± 3.4 [0.035 ± 0.013]	–

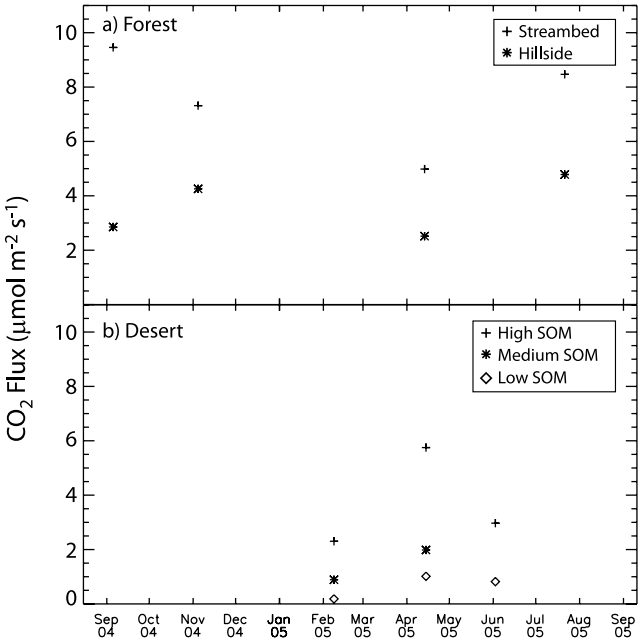

Figure 5. CO_2 flux rates (μmol m^{-2} s^{-1}) at the (a) forest and (b) desert field sites.

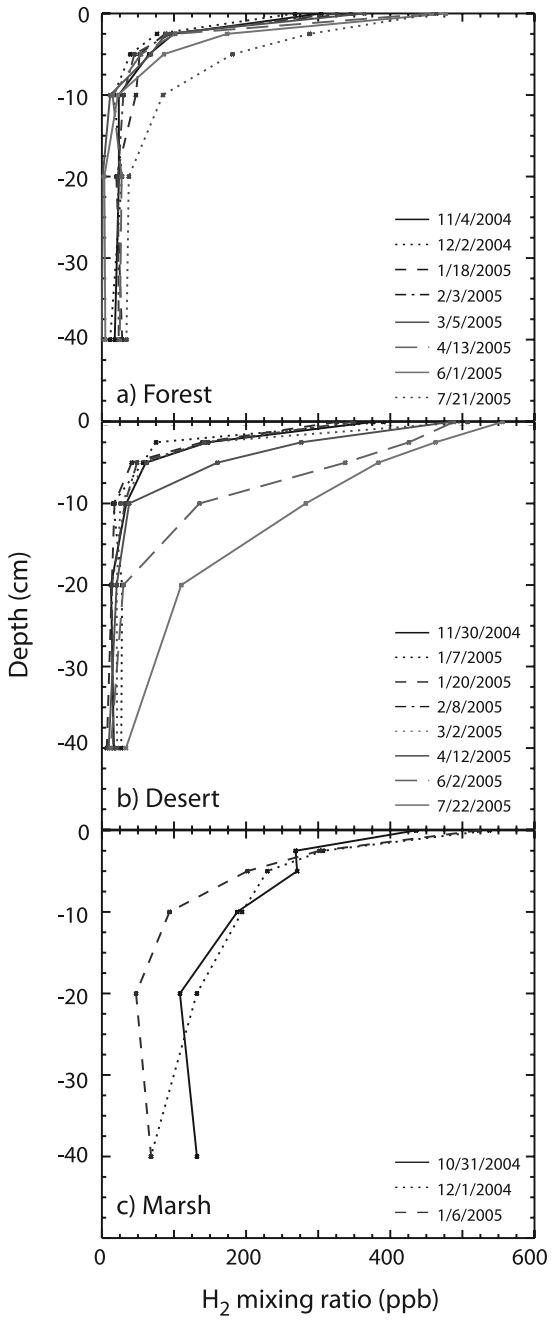

Figure 6. H_2 mixing ratio with depth at the (a) forest, (b) desert, and (c) marsh field sites. Each line represents the average of all soil profiles measured at each site. In Figure 6b, H_2 penetrates deeper into the soil from April to July 2005 because of drying and inactivation of the surface soil layers. The increased H_2 at 40 cm depth at the marsh field site (Figure 6c) may be due to anaerobic production of H_2 in saturated soils below our deepest soil gas sampler.

the flux of H_2 observed at the surface (Figure 8). After the litter layer was removed, the observed flux at the surface increased from -9.7 to -12.3 nmol m^{-2} s^{-1}. Each of the removed soil layers consumed more hydrogen than the intact soil profile (-24.4 and -18.9 nmol m^{-2} s^{-1} versus -12.3 and -12.8 nmol m^{-2} s^{-1}). At the desert site, the topmost vegetation and soil layers did not consume H_2. As layers of soil were removed, the observed surface H_2 flux increased from -6.0 to -9.7 to -14.4 nmol m^{-2} s^{-1}. This increase provides qualitative evidence that dry litter and surface soils normally limit the diffusion of atmospheric H_2 to deeper soil layers that are moist and metabolically active.

4. Modeling Diffusive Properties of Soils

[19] To demonstrate the role of diffusion in the uptake of H_2 by soils, we adapted the parameterization developed by *Smith-Downey* [2006] to describe H_2 uptake as a function of the diffusivity of soils (D_s) and biological uptake capacity (λ). In general, the flux of H_2 at the surface is proportional to the concentration gradient

$$F_{H_2} = D_s \frac{\partial [H_2]}{\partial z}\bigg|_{z = \text{soil\_surface}}, \quad (5)$$

where z is depth (cm). The gradient in $[H_2]$ with depth in the soil is driven by both the biological uptake of H_2 in the soil profile, and the diffusive structure of soils. It can be described by the diffusion equation with a first-order loss term

$$\frac{\partial [H_2]}{\partial t} = \frac{\partial}{\partial z}\left(D_s(z)\frac{\partial [H_2]}{\partial z}\right) - \frac{\lambda(z)}{\varepsilon}[H_2], \quad (6)$$

where t is time (s), z is depth (cm), D_s is the diffusivity of hydrogen in soil as a function of depth (cm^2 s^{-1}), λ is the biological uptake rate (s^{-1}), and ε is the fractional air space (unitless).

[20] The diffusivity of hydrogen in soils (D_s) varies with depth and is a function of the diffusivity of H_2 in air (D_g) and soil air filled porosity. Air filled porosity is primarily determined by soil structure and moisture content, which leads to a strong control of soil texture and saturation on the diffusivity of hydrogen in soils [*Yonemura et al.*, 1999, 2000b; *Smith-Downey et al.*, 2006]. The uptake of hydrogen by soils (λ) is biologically controlled and varies with soil moisture and temperature [*Fallon*, 1982; *Conrad and Seiler*, 1985; *Smith-Downey et al.*, 2006]. Using the finite difference solution to this model, we explored the effect of changes in D_s, and λ on the distribution of H_2 with depth and on surface flux rates (Figure 9).

[21] Assuming a constant D_s of 0.1 cm^2 s^{-1}, a surface H_2 mixing ratio of 530 ppb and an ε of 0.3, we tested the effect of decreasing the biological uptake capacity (λ) uniformly with depth from 5×10^{-2} s^{-1} to 5×10^{-4} s^{-1}. As λ decreases by 2 orders of magnitude, H_2 penetrates deeper into soils (Figure 9a) and as a consequence more soil volume is exposed to elevated levels of H_2. The net effect is a much smaller reduction in surface fluxes, with fluxes decreasing by only a factor of 6 from -38 nmol m^{-2} s^{-1} to -6 nmol m^{-2} s^{-1} (Figure 9b). Reducing the diffusivity of soils by a factor of 10 from 1.25×10^{-1} cm^2 s^{-1} to 1.25×10^{-2} cm^2 s^{-1} (and assuming a constant λ of 2.5×10^{-2} s^{-1} that is uniform with depth) results in shallower H_2 penetration into soils (Figure 9c), and decreases in surface flux rates (Figure 9d). The reduction in surface fluxes, however, is again smaller than the initial change in diffusivity (a

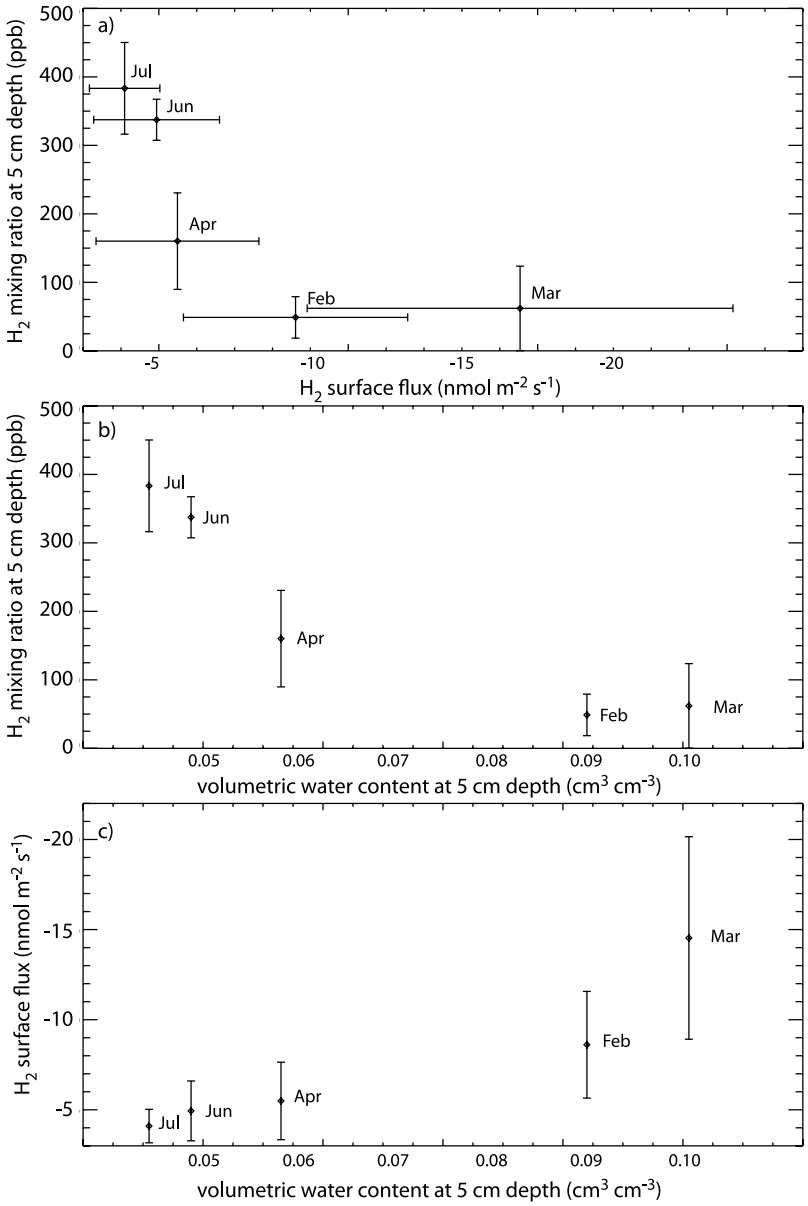

Figure 7. Steady state hydrogen mixing ratio at 5 cm depth for the desert field site between February and July 2004 plotted along with (a) the observed surface flux (nmol m^{-2} s^{-1}) and (b) the volumetric soil water content averaged at 5 cm depth. (c) The volumetric water content of soils versus observed surface flux of H_2 (nmol m^{-2} s^{-1}) for the same time period.

factor of 6 versus a factor of 10) (Figure 9d). Finally, to test the effect of inactive layer depth (d_i), we set λ of the surface soil layer to zero, and the remaining soil profile to 2.5×10^{-2} cm^{-1}. As d_i increased from 0 to 20 cm, H_2 penetrated deeper into the soil profile (Figure 9e) and surface fluxes rapidly decrease from -31 nmol m^{-2} s^{-1} to -2 nmol m^{-2} s^{-1} (Figure 9f).

5. Discussion and Conclusions

[22] Our field observations provide evidence that ecosystem type is not a strong controller of soil H_2 flux rates and that the vertical distribution of H_2 uptake capacity and diffusive properties of soils have important effects on surface flux rates. The rate of H_2 consumption was nearly equal at the forest and desert sites, suggesting that uptake rates in low productivity ecosystems such as deserts may not scale with net primary production or soil organic matter, key variables that have been used to describe spatial patterns of soil CO_2 fluxes. Our soil profile experiments demonstrated that the vertical distribution of H_2 uptake with depth changed over time in response to a decrease in soil moisture, which is consistent with previous work suggesting that H_2 uptake requires a minimum moisture level for microbial activation [*Fallon*, 1982; *Conrad and Seiler*, 1985; *Smith-Downey et al.*, 2006]. The profile measurements show that the surface layer of soil at the desert site became inactive with respect to hydrogen between March

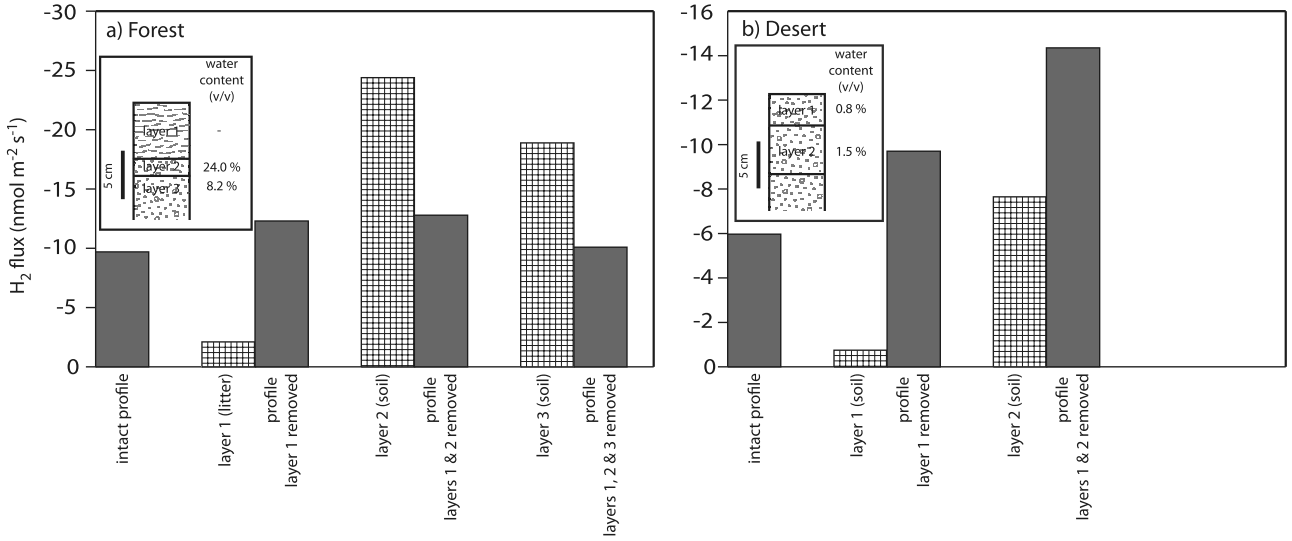

Figure 8. Soil removal experiments at the (a) forest and (b) desert field sites. Here, surface fluxes were measured, and successive layers of the soil profile were removed and placed in a separate sealed soil collar to determine the vertical distribution of uptake with depth. At the forest site (Figure 8a) we found that removing the surface litter layer (layer 1) increased the profile flux rate and that successive soil layers consumed more H_2 than the intact profile. Layer 1 (litter) was 6 cm deep with a bulk density of 0.017 g/cm^3, layer 2 was 1.5 cm deep with a bulk density of 0.83 g/cm^3, and layer 3 was 2.5 cm deep with a bulk density of 1.27 g/cm^3. At the desert site (Figure 8b) we found that removing surface layers of sand increased the profile flux rate and that the surface layer (layer 1) consumed relatively little H_2. Layer 1 was 3.5 cm deep with a bulk density of 0.79 g/cm^3 and layer 2 was 5 cm deep with a bulk density of 1.24 g/cm^3. The internal area of the soil collars was 0.0324 m^2.

and April, and that this inactive layer penetrated deeper through the soil profile through July. This corresponded with decreases in the surface flux of H_2, suggesting that the vertical distribution of H_2 uptake by microbes within the soil is important for the surface flux, and that this is controlled by soil moisture (Figure 7c).

[23] At all of our sites, the H_2 mixing ratio at depth appeared to be nonzero (Figure 6), which would suggest a steady state equilibrium between H_2 production and consumption in soils. We cannot rule out contamination during sample collection and analysis, but our data were corrected for the leak rates we observed in the lab. The local maximum observed at 40 cm depth at the marsh site in October, and the general higher steady state mixing ratio with depth at this site certainly suggests both production and consumption of H_2 occurring simultaneously in these soils.

[24] At the forest streambed site, a flooding event deposited $\sim$ 5 cm of sediment and litter over our collars in January 2005. This led to a dramatic decrease in H_2 fluxes, which subsequently recovered by April 2005. This suggests that soil disturbance, particularly disturbance that impedes the diffusion of H_2 into soils, is a powerful local control on soil H_2 uptake.

[25] Generally, there was little observable difference between fluxes at the forest and desert sites, but the marsh site exhibited slightly lower fluxes. We hypothesize that this is primarily due to differences in soil structure. The soils at the forest and desert sites were relatively porous, whereas the marsh was dominated by fine-grained, clay-rich, and less porous soil.

[26] At the desert site, we designed our experiments to test the effect of organic carbon on H_2 fluxes by placing our soil collars along a gradient in SOM and vegetation from directly under oak shrubs to bare sand. Although CO_2 fluxes were substantially higher under the oak, and decreased as we moved to bare sand, no such trend was apparent in the H_2 flux data. This suggests that soil organic carbon content is not a strong controller of H_2 uptake, which is similar to patterns that have been observed for the uptake of methane by desert soils [*Striegl et al.*, 1992]. *Yonemura et al.* [1999] reported increased H_2 fluxes after organic material was plowed into study plots, but the physical disturbance of plowing may have increased the diffusivity of H_2 into the soil. *Smith-Downey et al.* [2006] report that in laboratory experiments, soil from the boreal forest, with very high organic carbon content (39%) has a higher uptake capacity than soils from the same desert site studied here. It appears that if soil organic matter does play a role in the uptake of H_2, it is secondary to other factors such as diffusion and moisture availability.

[27] Soil removal experiments showed that the litter layer at the forest site had an H_2 flux that was nearly zero. We attribute the small flux we did observe to a small amount of soil that was intermixed with the litter in the soil collar. Once the litter layer was removed, the flux at the surface increased. This is consistent with the removal of a diffusive barrier, which enhances the supply of H_2 to the underlying soils, and is similar to observations of CO deposition onto soils after litter removal [*Sanhueza et al.*, 1998]. Layers of soil that we removed from the soil profile had progressively higher flux rates when we measured them in a sealed collar.

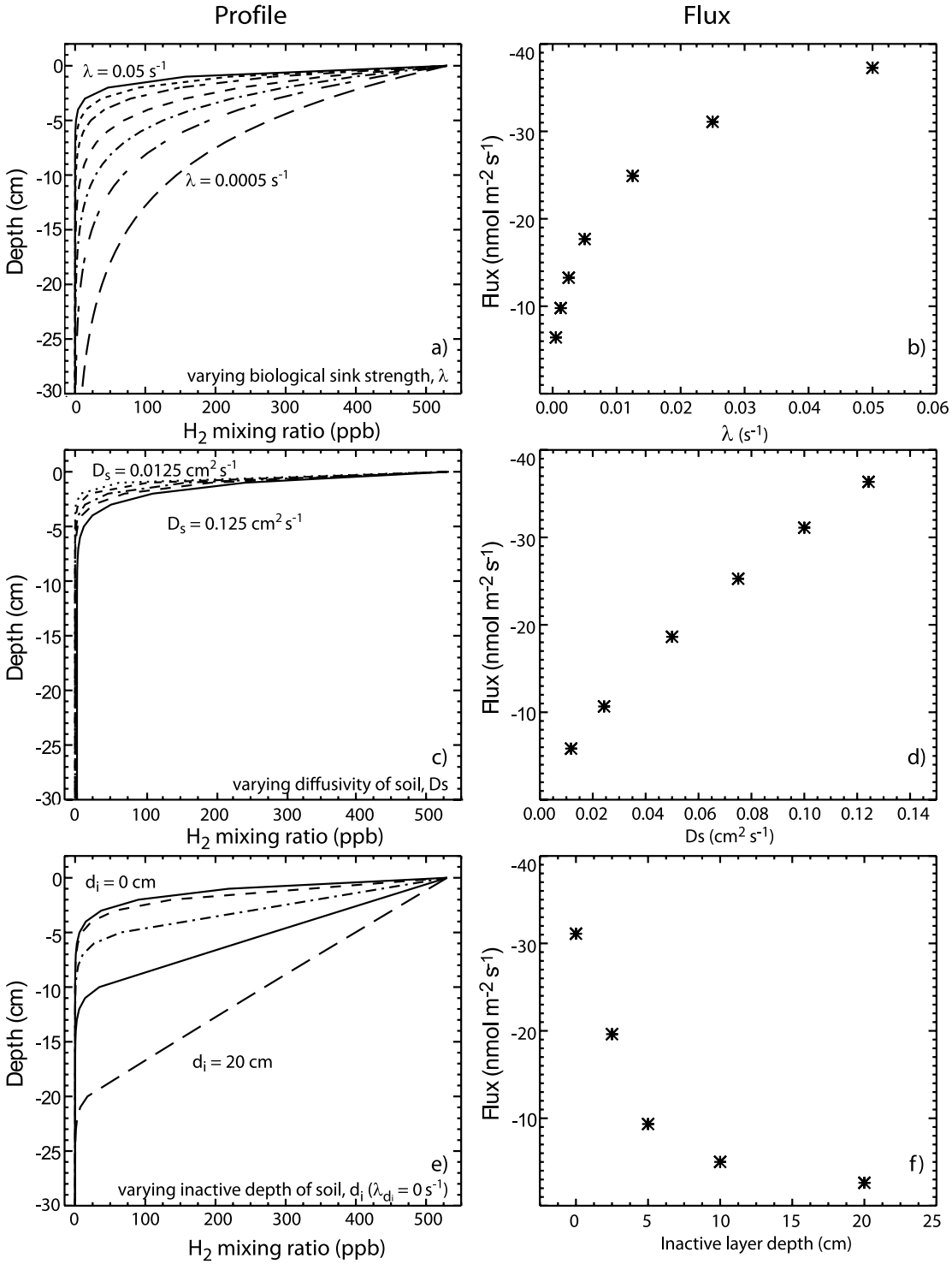

Figure 9. Sensitivity experiments for changes in the biological uptake capacity and diffusivity of soils. (left) The H_2 mixing ratio with depth in the soil profile under different conditions, and (right) the associated changes in the surface flux rates. (a) Reducing the strength of biological uptake (λ) uniformly in the soil profile causes H_2 to penetrate deeper into the soil profile. (b) As λ increases, surface fluxes increase rapidly at first, then more slowly as the total flux becomes diffusion limited. (c) Decreasing the diffusivity (D_s) of H_2 in soils (analogous to filling pore space with water) results in an increased concentration gradient at the surface and shallower penetration of H_2 into soils. (d) As D_s increases, fluxes at the surface increase. (e) Increasing the depth of an inactive layer of soil (d_i), where $\lambda = 0\ s^{-1}$, results in a smaller concentration gradient at the surface and a shallower penetration of H_2 into soils. (f) As d_i increases, the fluxes at the surface rapidly decrease because consumption of H_2 becomes limited by diffusion through the inactive layer.

In some cases the flux of H_2 into the removed soil layer was larger than that of the intact profile. In removing the soil layers from the surface and transferring them to the sealed collar, we disturbed the soil structure and thus greatly enhanced the exposure of soil microbes to atmospheric H_2 levels.

[28] At the desert site, we observed an inactive layer of soil at the top of the profile in our soil removal experiments. When this layer was removed, the surface flux of H_2 increased from -6 nmol m^{-2} s^{-1} to -10 nmol m^{-2} s^{-1}. After a second layer of soil was removed, the surface flux increased to -14 nmol m^{-2} s^{-1}. This experiment highlights the importance of the diffusive structure and vertical distribution of H_2 uptake capacity on surface flux rates. As soil that did not consume H_2 was removed, a diffusive barrier was also removed, which increased the availability of H_2.

[29] Modeling analysis provides further evidence that soil diffusivity and the vertical distribution of biological uptake interact to regulate surface flux rates. Because the system is diffusion limited, however, it is more sensitive to changes in the diffusive properties of soils than to changes in the biological uptake. Our results show that if λ decreases by a factor of 100 (from 5×10^{-4} cm s^{-1} to 5×10^{-2} cm s^{-1}) the surface fluxes are reduced by only a factor of 6 (-38 nmol m^{-2} s^{-1} to -6 nmol m^{-2} s^{-1}). In contrast, increasing the inactive layer depth from 0 to 5 cm increases the diffusive barrier to biological uptake and reduces surface fluxes from -31 nmol m^{-2} s^{-1} to -10 nmol m^{-2} s^{-1}, or 68%. Our observations show that, as even during summer the deep subsurface soil layers retained enough soil moisture to facilitate biological uptake. Most of the flux variability observed at this site appeared to be related to variations in the inactive layer depth. The increases in H_2 penetration depth we observed during summer (Figure 6b) were qualitatively similar in shape to that expected from an increasing surface inactive layer (Figure 9c). This may explain why observations at the forest hillside and marsh sites did not vary substantially over the course of the growing season. As long as the entire soil profile is consuming H_2 and remains well drained, variability in λ will not drive large changes in the surface flux rates. This also implies that in a future H_2 emissions scenario, if the diffusive properties and λ of soils remain the same, the flux of H_2 into soils will decrease linearly with concentration. If λ increases in response to increasing H_2, the effect on surface fluxes will be small because of compensating decreases in the penetration of H_2 into the soil profile.

[30] Our results suggest that both the diffusive properties of soil, which regulate H_2 supply to soil microbes, and the vertical distribution of biological uptake control the surface fluxes of H_2. These results are consistent with previous observations from several groups [*Conrad and Seiler*, 1985; *Yonemura et al.*, 1999, 2000a, 2000b; *Smith-Downey et al.*, 2006] and we propose that in order to predict future changes hydrogen fluxes, it is necessary to model how both the diffusive properties of soils (e.g., changes in snow cover or soil moisture) and rates of microbial uptake respond to changing environmental conditions.

[31] **Acknowledgments.** N.S.D.thanks J. Leadbetter for lab and instrument use, X. Xu and G. Cane for assistance with the elemental analyzer at UC Irvine, L. Welp for assistance with field equipment design, and N. Downey for assistance in the field. We also thank colleagues working within the University of California Natural Reserve System, including B. Bretz, B. Berger, and M. Hamilton for their assistance in establishing and monitoring field sites. N.S.D. was supported by the NCER STAR program funded by the U.S. EPA. J.T.R. acknowledges support from University of California Irvine's School of Physical Sciences Dean's Innovation Fund. This work was also supported by a generous gift from General Motors and William Davidow and family.

References

Conrad, R., and W. Seiler (1985), Influence of temperature, moisture, and organic carbon on the flux of H_2 and CO between soil and atmosphere: Field studies in tropical regions, *J. Geophys. Res.*, *90*, 5699–5709, doi:10.1029/JD090iD03p05699.

Fallon, R. D. (1982), Influences of pH, temperature, and moisture on gaseous tritium uptake in surface soils, *Appl. Environ. Microbiol.*, *44*, 171–178.

Gerst, S., and P. Quay (2001), Deuterium component of the global molecular hydrogen cycle, *J. Geophys. Res.*, *106*, 5021–5031, doi:10.1029/2000JD900593.

Hauglustaine, D. A., and D. H. Ehhalt (2002), A three-dimensional model of molecular hydrogen in the troposphere, *J. Geophys. Res.*, *107*(D17), 4330, doi:10.1029/2001JD001156.

Lallo, M., T. Aalto, T. Laurila, and J. Hatakka (2008), Seasonal variations in hydrogen deposition to boreal forest soil in southern Finland, *Geophys. Res. Lett.*, *35*, L04402, doi:10.1029/2007GL032357.

Novelli, P. C., P. M. Lang, K. A. Masarie, D. F. Hurst, R. Myers, and J. W. Elkins (1999), Molecular hydrogen in the troposphere: Global distribution and budget, *J. Geophys. Res.*, *104*, 30,427–30,444, doi:10.1029/1999JD900788.

Price, H., L. Jaegle, A. Rice, P. Quay, P. C. Novelli, and R. Gammon (2007), Global budget of molecular hydrogen and its deuterium content: Constraints from ground station, cruise, and aircraft observations, *J. Geophys. Res.*, *112*, D22108, doi:10.1029/2006JD008152.

Rahn, T., J. Eiler, N. Kitchen, J. E. Fessenden, and J. T. Randerson (2002), Concentration and dD of molecular hydrogen in boreal forests: Ecosystem-scale systematics of atmospheric H_2, *Geophys. Res. Lett.*, *29*(18), 1888, doi:10.1029/2002GL015118.

Rahn, T., J. Eiler, K. A. Boering, P. O. Wennberg, M. C. McCarthy, S. Tyler, S. Schauffler, S. Donnelly, and E. Atlas (2003), Extreme deuterium enrichment in stratospheric hydrogen and the global atmospheric budget of H_2, *Nat.*, *424*, 918–921, doi:10.1038/nature01917.

Rhee, T. S., C. A. M. Brenninkmeijer, and T. Rockmann (2006), The overwhelming role of soils in the global atmospheric hydrogen cycle, *Atmos. Chem. Phys.*, *6*, 1611–1625.

Sanhueza, E., Y. Dong, D. Scharffe, J. M. Lobert, and P. J. Crutzen (1998), Carbon monoxide uptake by temperate forest soils: The effects of leaves and humus layers, *Tellus Ser. B*, *50*, 51–58, doi:10.1034/j.1600-0889.1998.00004.x.

Schultz, M. G., T. Diehl, G. P. Brasseur, and W. Zittel (2003), Air pollution and climate-forcing impacts of a global hydrogen economy, *Science*, *302*, 624–627, doi:10.1126/science.1089527.

Smith-Downey, N. (2006), Soil uptake of molecular hydrogen and remote sensing of soil freeze and thaw, Ph.D. thesis, 116 pp., Calif. Inst. of Technol., Pasadena, Calif.

Smith-Downey, N., J. T. Randerson, and J. Eiler (2006), Temperature and moisture dependence of soil H_2 uptake measured in the laboratory, *Geophys. Res. Lett.*, *33*, L14813, doi:10.1029/2006GL026749.

Striegl, R. G., T. A. McConnaughey, D. C. Thorstenson, E. P. Weeks, and J. C. Woodward (1992), Consumption of atmospheric methane by desert soils, *Nat.*, *357*, 145–147, doi:10.1038/357145a0.

Tromp, T. K., L. R.-Shia, M. Allen, J. Eiler, and Y. Yung (2003), Potential environmental impact of a hydrogen economy on the stratosphere, *Science*, *300*, 1740–1742, doi:10.1126/science.1085169.

Warwick, N. J., S. Bekki, E. G. Nisbet, and J. A. Pyle (2004), Impact of a hydrogen economy on the stratosphere and troposphere studied in a 2-D model, *Geophys. Res. Lett.*, *31*, L05107, doi:10.1029/2003GL019224.

Western Regional Climate Center (2007), Western U. S. Climate Historical Summaries, http://www.wrcc.dri.edu/Climsum.html, West. Reg. Clim. Cent., Reno, Nev.

Xiao, X., et al. (2007), Optimal estimation of the soil uptake rate of molecular hydrogen from the Advanced Global Atmospheric Gases Experiment and other measurements, *J. Geophys. Res.*, *112*, D07303, doi:10.1029/2006JD007241.

Yonemura, S., S. Kawashima, and H. Tsuruta (1999), Continuous measurements of CO and H_2 deposition velocities onto an andisol: Uptake control by soil moisture, *Tellus Ser. B*, *51*, 688–700.

Yonemura, S., S. Kawashima, and H. Tsuruta (2000a), Carbon monoxide, hydrogen, and methane uptake by soils in a temperate arable field and

a forest, *J. Geophys. Res.*, *105*, 14,347–14,362, doi:10.1029/1999JD901156.

Yonemura, S., M. Yokozawa, S. Kawashima, and H. Tsuruta (2000b), Model analysis of the influence of gas diffusivity in soil on CO and H_2 uptake, *Tellus Ser. B*, *52*, 919–933.

J. M. Eiler, Geological and Planetary Sciences, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125, USA.

J. T. Randerson, Department of Earth System Science, University of California Irvine, Croul Hall, Irvine, CA 92697, USA.

N. V. Smith-Downey, School of Engineering and Applied Sciences, Harvard University, Pierce Hall, 29 Oxford Street, Cambridge, MA 02138, USA. (nicolevdowney@gmail.com)